HEAVY OXYGEN ISOTOPE DIFFUSION IN FIRN

a Thesis

Presented in partial fulfilment
for the degree
Bachelor of Science

by
Gary Lee LaRue

The Ohio State University
1983

Approved I. M. Williams

Advisor
Department of Geology & Mineralogy

ABSTRACT

The model of Bow (1982) for isotopic diffusion in polar firn is refined and numerically modelled. It appears to work well but an accurate test against available data is not possible because the effects of variation in original deposition cannot be segregated with confidence from those due to diffusion.

ACKNOWLEDGEMENTS

I would like to thank Ian M. Whillans for supplying the topic for this paper and all of the help given in the course of its execution. The patience and diligence displayed by him are greatly appreciated. I would also like to thank Henry Brecher and Joe Kostecka and other staff and students of the Ohio State University Department of Geology and Institute of Polar Studies who have helped and encouraged me in the completion of this project.

The typing of the final manuscript and drafts was done by Mary LaRue and Patty Royer.

TABLE OF CONTENTS

LIST OF TABLES

page

LIST OF FIGURES

INTRODUCTION

PURPOSE

The interpretation of climatic data obtained from ice cores depends on the ability to understand the physical processes taking place after deposition of an annual layer of snow and during its subsequent transformation into ice. As each annual layer becomes more deeply buried, the seasonal cycle in oxygen isotopic ratio diffuses and the seasonal record becomes less marked. When snow is fresh diffusion is at its peak, as firn changes into solid ice the process slows and virtually stops. This paper reviews a theory for the diffusion of seasonal isotopic cycles and presents the results of a computer simulation in the upper twenty meters of firn. This simulation is more accurate and takes account of more processes than have been considered previously. The results of the simulation are then compared with data collected at Pit 8D in Greenland (see location map next page) by Whillans and others in 1981 in the course of study of the Greenland ice sheet.

PREVIOUS WORK

Previous work in this field was done by Johnsen (1977) who proposed that vapor diffusion caused the smoothing of $\delta\,^{18}O$ profiles. This study utilizes and refines a mathematical model proposed by Bow (1982) for the smoothing of $\delta\,^{18}O$ profiles by vapor diffusion.

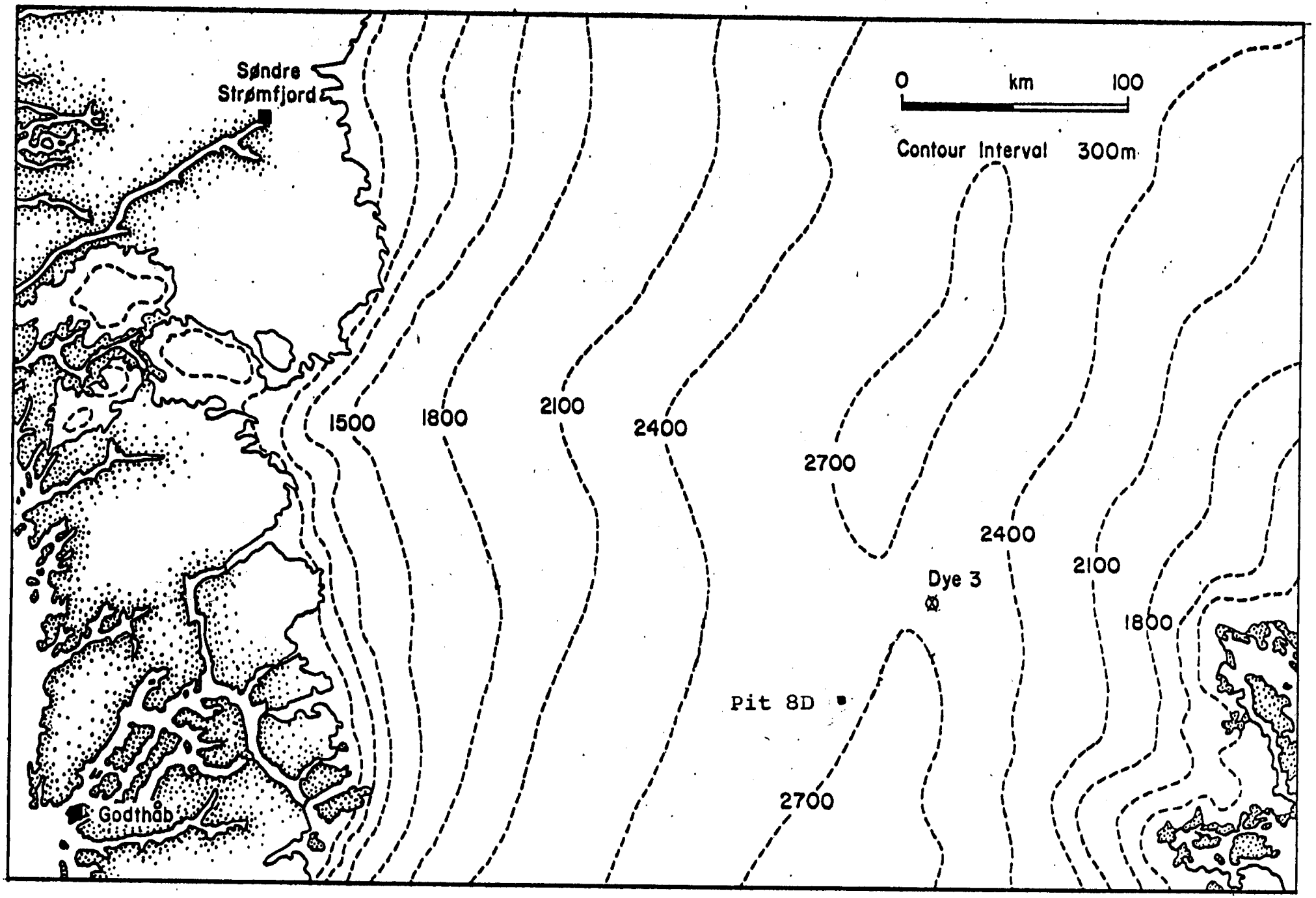

Søndre
Strømfjord
0
km
100
Contour Interval 300m
1500
1800
2100
2400
2700
2400
2100
1800
Dye 3
Pit 8D
2700
Godthåb

FIGURE 1

Location map for Pit 8D where data used for this study was collected by Whillans and others in 1981. Pit 8D was excavated and cored to a depth of 18 meters. The elevation contours on the map were obtained before Whillans' Survey was complete. Pit 8D is at 2701 meters above sea level.

THEORY

Water vapor like most gases, diffuses from areas of high concentration to areas of low concentration. Such diffusion is described by well-established theory in the case of stagnant unobstructed air. This vapor flux transports and mixes molecules such as ^{18}O and ^{16}O. Following Bow (1982) we propose that the main agent for the smoothing of delta-^{18}O profiles in firn is vapor diffusion. This is described by Fick's law (Atkins, 1978):

$$F = - D_f \frac{\partial N_v^{18}}{\partial z} \qquad (1)$$

F represents the flux of $H_2{}^{18}O$ molecules moving from high to low concentration, D_f represents the diffusivity of the firn, N_v^{18} represents the molar concentration of $H_2{}^{18}O$ in the vapor and Z represents the depth.

This process can be viewed as molecules moving along a concentration gradient. Consider a number of closely spaced horizons in the firn, each of which may contain a different relative population of $H_2{}^{18}O$. A certain horizon within the firn, horizon (B) contains a population of $H_2{}^{18}O$ and $H_2{}^{16}O$. If this layer were isolated the ratio would remain constant. Each layer, however, is in contact with and connected through pore space to layers above, below and ultimately to the atmosphere. As each of these layers contain different concentrations of the two oxygen isotopes there exist concentration gradients on either

side of horizon (B). This will cause a change in the concentration of $H_2{}^{18}O$ and delta-^{18}O in horizon (B). If the layer above horizon (B) (horizon (A)) has lower delta-^{18}O then $H_2{}^{18}O$ would show net diffusion towards horizon (A). If the layer below horizon (B) also had lower delta-^{18}O there would be a concentration gradient of opposite vector than that between horizon (A) and horizon (B).

If the flux of molecules below a layer differs from that above a change in the concentration of $H_2{}^{18}O$ in the layer will occur. That is:

$$\frac{\partial N_f^{18}}{\partial t} = -\frac{\partial F}{\partial z} \qquad (2)$$

$N_f{}^{18}$ represents the molar concentration of $H_2{}^{18}O$ in both vapor and solid while t represents time.

The preceding two equations represent the factors controlling diffusion between layers. The combination of equations (1) and (2) yields:

$$\frac{\partial N_f^{18}}{\partial t} = \frac{\partial}{\partial z}\left(D_f \frac{\partial N_v^{18}}{\partial z}\right) \qquad (3)$$

This equation shows that the change in $H_2{}^{18}O$ concentration in a layer in firn over time is a function of the gradient of the flux of ^{18}O atoms in the vapor. Equation (3) describes the primary processes of oxygen isotopic diffusion in air.

The existence of an ice matrix in firn complicates the vapor diffusion mechanism in two important ways. In the first instance presence of the ice matrix is a physical barrier to the movement and molecular exchange of ^{18}O and ^{16}O.

The second factor which slows vapor diffusion and smoothing rates is molecular exchange between the water vapor and the ice matrix (as the pores reach close-off this becomes more important as does solid ice molecular diffusion). In firn the water vapor in pores is modeled as being in continuous dynamic equilibrium with the ice matrix. In this case the ice slows the mixing by holding the individual molecules in the crystal lattice for extended periods. While the molecules are trapped they are not greatly affected by solid diffusion and of course not at all by vapor diffusion. The molecules are out of circulation until they sublimate back into the vapor phase.

These are the essential concepts in our model of isotopic diffusion in firn. Diffusivity, the above mentioned blockage effect and storage of molecules, are influenced by local firn conditions such as depth, temperature or density. We will now proceed to add these effects to the model.

The significance of the blockage effect is that it

reduces the available diffusion pathways (tortuosity if hard to quantify and will be ignored here). Pore space volume is a measureable local condition that can be used to calculate the blockage effect on vapor transport. Large pore space volume encourages diffusion. The pore volume is related to the density and depth of the layer. The density increases as the firn becomes compacted with increasing snow deposition at the surface. Thus, as each seasonal layer becomes more deeply buried through time, the smoothing rate abates due to the slower vapor diffusion. The relative pore volume is described by:

$$P_s = 1 - \frac{\rho_f}{\rho_i} \qquad (4)$$

P_s represents the proportion of pore space. ρ_f the density of firn and ρ_i the density of ice. Firn diffusivity D_f is considered as being related to the diffusivity of water vapor in open air. D_a in proportion to the space available for diffusion:

$$D_f = D_a \cdot P_s \qquad (5)$$

D_a varies most notably with temperature. Note that vapor diffusion goes to zero for solid ice and nearly to that of free air at low firn densities.

The concentration of ^{18}O is usually expressed with reference to the ^{16}O concentration using the delta-^{18}O

value. The relative amount of each species is useful in determining climatic conditions at the time the firn fell as snow. Since the amount of ^{16}O is so much greater than ^{18}O the ratio is not easily expressed directly. This is resolved by comparing the ^{16}O: ^{18}O ratio to the same ratio in a standard sample of sea-water, SMOW (Standard Mean Ocean Water). This is then expressed as delta-^{18}O:

$$\delta^{18}O = \left(\frac{N^{18}}{N^{16}} - \frac{N^{18}}{N^{16}}_{SMOW}\right) \Big/ \frac{N^{18}}{N^{16}}_{SMOW} \qquad (6)$$

$\frac{N^{18}}{N^{16}}$ SMOW, is the ratio of molar concentration of ^{16}O to ^{18}O in SMOW.

$\frac{N^{18}}{N^{16}}$, is the ratio of molar concentration of ^{16}O to ^{18}O in firn. This relation can be expressed in terms of delta values and the densities of firn and water vapor. Re-writing equation (6) above in terms of N_f^{18} and N_v^{18}

$$N_f^{18} = (\delta_f + 1)(N_f^{16})\left(\frac{N^{18}}{N^{16}}_{SMOW}\right) \qquad (7)$$

$$N_v^{18} = (\delta_v + 1)(N_v^{16})\left(\frac{N^{18}}{N^{16}}_{SMOW}\right) \qquad (8)$$

Where δ_f and δ_v are Delta ^{18}O values for firn and vapor respectively. This expression for N_f^{18} and N_v^{18} is now substituted into equation (3). Note that the molar concentration of N_f^{16} is, to 0.2% equal to the concentration of both of the isotopic species combined $N_f^{16 + 18}$ CRC page B-257 (1982).

This yields:

$$\frac{\partial (\delta_f + 1) N_f^{16+18}}{\partial t} = \frac{\partial}{\partial z} \left(D_f \frac{\partial (\delta_v + 1) N_v^{16+18}}{\partial z} \right) \quad (9)$$

The molar concentration of firn and vapor related to density are:

$$N_f = \frac{\rho_f}{MW} \quad (10)$$

$$N_v = \frac{\rho_v}{MW} \quad (11)$$

Where ρ_f is the mass density of the firn and ρ_v is the mass density of the vapor. MW is the molecular weight of water. Rewriting equation (9):

$$\frac{\partial (\delta_f + 1) \rho_f}{\partial t} = \frac{\partial}{\partial z} \left(D_f \frac{\partial (\delta_v + 1) \rho_v}{\partial z} \right) \quad (12)$$

δ_f and δ_v may differ due to equilibrium isotopic fractionation according to:

$$\delta_f = \delta_v + \Delta\delta \quad (13)$$

is the isotopic fractionation term. In the Bow (1982) model this is taken as constant regardless of time, temperature or distance.

Assuming $\Delta\delta$ is constant the terms $\frac{\partial \Delta\delta_f}{\partial z}$ and $\frac{\partial \Delta\delta_v}{\partial z}$ are taken as zero. This allows us upon differentiation of δ_f and δ_v to drop the subscripts. P_f is held constant for a first approximation. After these steps are taken the equations are combined and simplified. The final

equation taking into account all of these factors and neglecting second order terms is:

$$\frac{\partial \delta}{\partial t} = \frac{D_f \rho_v}{\rho_f} \cdot \frac{\partial^2 \delta}{\partial z^2} \qquad (14)$$

(Bow, 1982)

ρ_v is defined as follows using the perfect gas relation:

$$\rho_v = \frac{\underline{P} \cdot MW}{R \cdot T} \qquad (15)$$

MW is the molecular weight of the water vapor, $\underline{P}$ is the partial pressure of water vapor in air, R is the gas constant and T is the absolute temperature.

To illustrate the meaning of our model to this point we substitute into equation (14) expressions for density, pressure and diffusivity. This shows the smoothing rate in terms of elementary parameters and previously defined relations for D_f (equation (5)) and P_s (equation (4)).

The result of combining equations (4) (5) (14) and (15) is:

$$\frac{\partial \delta}{\partial t} = \frac{D_a \left(1 - \rho_f/\rho_i\right) \underline{P} \cdot MW}{\rho_f \cdot R \cdot T} \cdot \frac{\partial^2 \delta}{\partial z^2} \qquad (16)$$

Consider each variable in this equation in turn (while the others are held constant).

D_a, the diffusivity of water vapor in air is temperature dependent according to Geiger and Poirer, (1973, page 467):

$$D_a = 0.0371 \times (T + 273.16)^{1.75} \qquad (17)$$

D_a is much greater at higher temperatures and as D_a decreases the smoothing rate, $\frac{\partial \delta}{\partial t}$, also decreases.

The relative amount of pore space, $1-\rho_f/\rho_i$ is also important, Ice density, ρ_i , is constant while the value of ρ_f , varies with time. As the firn becomes more deeply buried and compacted the relative volume of pore space decreases. Note that ρ_f , also appears in the denominator. This factor allows for even slower smoothing rates at higher densities for exchange. As ρ_f , increases the smoothing rate decreases.

The partial pressure of water vapor in air, $\underline{P}$ also varies with temperature. As the temperature in the firn changes so does $\underline{P}$ (Magnus' formula in Iribane and Godson, 1973, p. 63):

$$\text{Log}_{10}\underline{P} = 10.5553 - 2667/(T - 0.16) \qquad (18)$$

The 0.16 represents an error in the Iribane and Godson version concerning the definition of absolute temperature.

Table I contains typical values and sources for parameters used in the solution of the model.

TABLE I

EXAMPLES OF TYPICAL PARAMETERS USED IN CALCULATION OF NEW $\delta^{18}O$ VALUES.

Parameter		Source	Temp K	Value	Unit
$\underline{P}$	(water vapor pressure over ice)	CRC (1983) page D-167	253 263 272	103 260 561	$N\ m^{-2}$
ρ_v	(density of water vapor)	Perfect Gas Law and $\underline{P}$	253 263 272	8.8×10^{-4} 2.1×10^{-3} 4.5×10^{-3}	kgm^{-3}
ρ_f	(density of firn)	Typical Value		400	kgm^{-1}
ρ_i	(density of ice)	Typical Value		920	kgm^{-3}
D_a	(diffusivity of water vapor in air)	Geiger & Poirier (1973)	253 263 272	1.9×10^{-5} 2.0×10^{-5} 2.1×10^{-5}	$m^2 s^{-1}$
D_f	(diffusivity of water vapor in firn)	$D_f = D_a \cdot \left(1 - \frac{\rho_f}{\rho_i}\right)$	253 263 272	1.0×10^{-5} 1.1×10^{-5} 1.2×10^{-5}	$m^2 s^{-1}$
C	(Effective Diffusivity water vapor in firn)	From Above	253 263 272	2.6×10^{-11} 5.8×10^{-11} 1.4×10^{-11}	$m^2 s^{-1}$

EFFECT OF SIMPLIFICATIONS AND ASSUMPTIONS

Of the two types of simplifications and assumptions made in this model, mathematical and geological, the mathematical are the most negligable and can be ignored. The geological assumptions though can have very striking effects.

This model does not allow for the compaction of the individual sampled horizons as it passes forward through time. This shows up in two ways. The measured layers are thinner than the modelled layers. The older sesonal horizon contains more of the annual delta cycle than those which have been modelled. For this reason we compare the amplitude of the $\delta\,^{18}O$ cycles.

The densification of the firn though does have an effect on the model since ρ_f appears in the effective diffusivity relation twice, as outlined in appendix A, the numerical solution. This effect causes the modelled values to be larger than they should. The open pore space is modelled as larger than it should be, and as the horizon passes forward through time the discrepancy becomes larger. This can be important were the compaction to happen instantaneously. In our case we only actually

predict what occurs over 10 years in the upper two meters of firn. The uncompacted layer is then compared with a compacted layer 10 years old at twenty meters depth. When tested against a program taking account of compaction the discrepancies are fairly small.

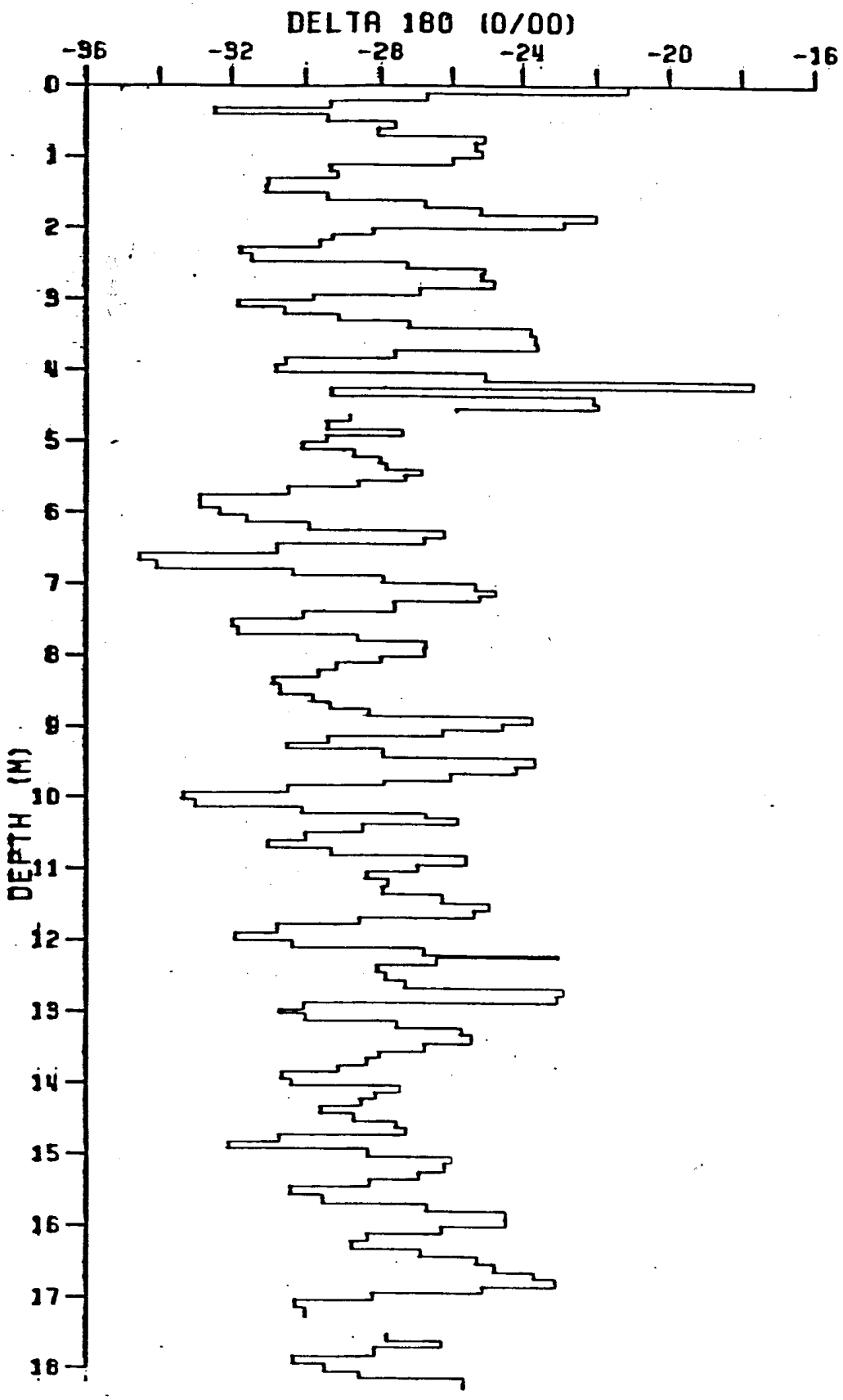
RESULTS

The results of this model compare closely to those actually obtained at Pit 8D near Dye 3 in Greenland. No direct comparison can be made however with existing data. This is because there is no reliable way to separate the variation in original deposition from later vapor diffusion effects. If the climate were totally predictable we could make a valid comparison of modelled and actual $\delta^{18}O$ profiles. There is the possibility of returning in 1991 to compare my predictions with actual profiles. The former will never occur, we will have to wait for the latter situation to present itself for a true idea of how the model works.

Compare the graphs in Figures 2 and 3. The data used for the modelling are taken from the measured ^{18}O values for the upper 2 meters and diffusion is simulated in the future (increasing depth). We follow the upper two meters as it becomes buried and vapor diffusion occurs. The graph produced gives a view of how the layer modelled should appear over time. The two graphs are not directly comparable but the amplitude of the middle portion of the cycle decays with time. This decay is similar to that observed in the firn profile (Figure 2).

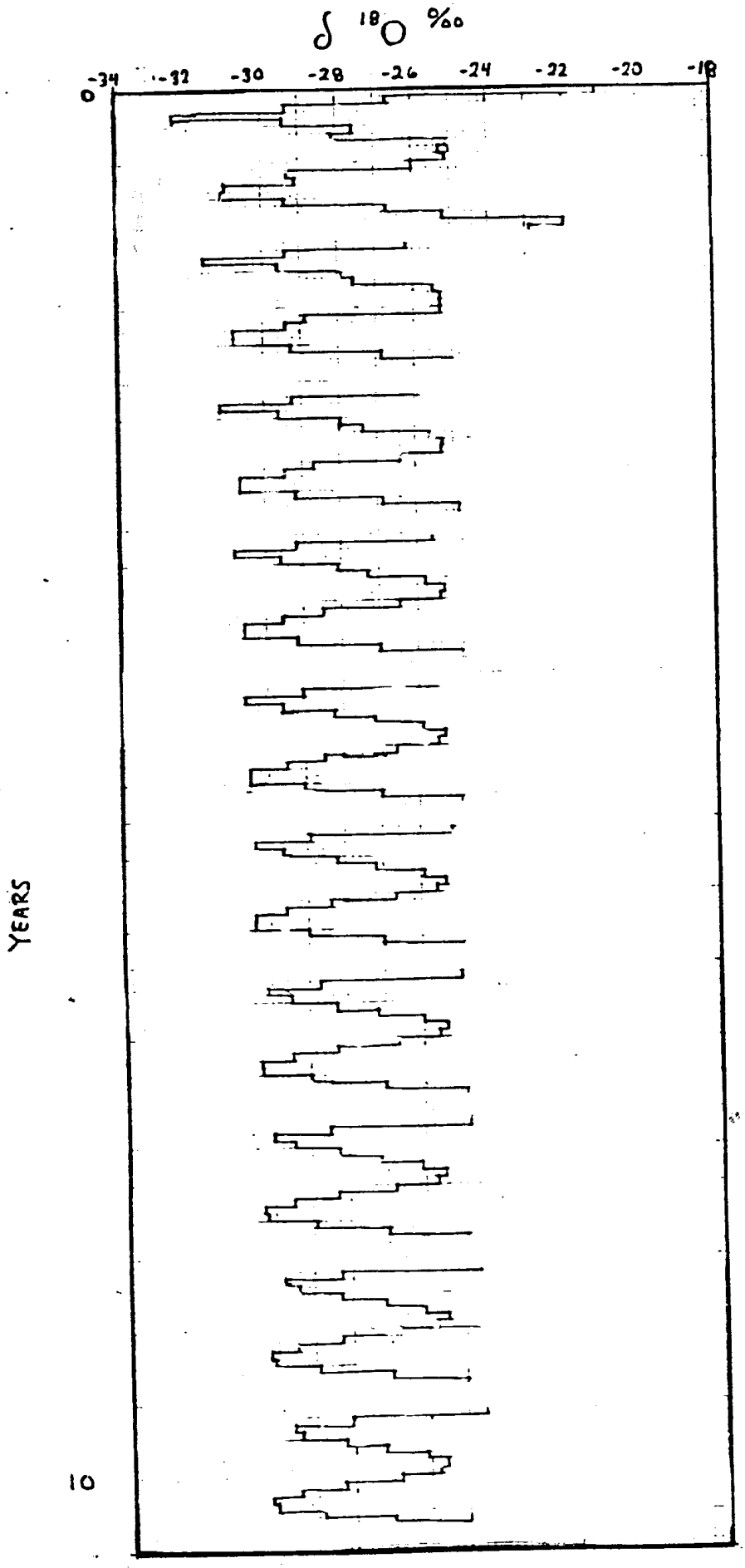
Page 17 is missing from the original.

FIGURE 2



Graph of $\delta^{18}O$ for measured values at Pit 8D

FIGURE 3



Modelled $\delta^{18}O$ from original values at Pit 8D

CONCLUSION

The vapor diffusion model predicts the smoothing of delta-^{18}O profiles with good result. The profiles which are produced by the model match reasonably with the actual profiles as measured in the field. The modelled values cannot be expected to match perfectly as the comparison is made between a two meter layer modelled over several years and a layer of approximately the same age but deposited at a different time. Also conditions in the firn such as temperature and density can differ greatly over only a few vertical centimeters. This leads to local variations in diffusion which are not modelled here. There may be other factors such as meltwater percolation which are not included in our model. Possible weather conditions are numberless, here we have modelled the most obvious temperature effects.

Short term temperature fluctuations can cause important changes in the diffusivity in certain strata in the firn. Temperature at snow deposition is the dominant control on original snow conditions. The snow if it is wet or becomes warmed while near the surface can form an impervious ice barrier to vapor diffusion. A snow of extremely low pore volume causes P_s to be very small,

inhibiting vapor diffusion greatly. The modelling would be more accurate if the density were accurately known.

Access to actual temperature in the firn over time would ensure that evaluation of effective diffusivity was accurate. This would increase confidence in the results since the diffusivity is very temperature sensitive.

The model takes account of temperature as a function of depth and time. Temperature profiles are generated by the program. This profile matches temperature profiles measured by Benson (1962) in Greenland. These generated curves are a fair first approximation but use of in situ measured temperatures would be much better. A permanent high density array of temperature sensors would be best. The resulting data would help address questions whether our calculations are not accurate in allowing for the temperature effect. These additional data may not change the calculated $\delta^{18}O$ values but nonetheless would increase confidence in the results and rule out one possible source for error.

A density profile on scale of 1 cm or less would identify possible closed-off firn layers blocking diffusion pathways on a locally important scale. These additional data would make the model more accountable to the geology

of the situation. The closed off layers block diffusion pathways and disrupt the vapor movement. These effects need to be dealt with in future work.

Accurate check of calculated values requires resampling of the same location in the future. In this way we can check our modelled horizon against itself after a number of years and see if the predictions were correct.

The vapor diffusion model of Bow (1982) is an important link toward our eventual understanding of firn metamorphism. The results of this study help to define the future direction to be taken in the solution of this problem.

APPENDIX A

NUMERICAL SOLUTION

To translate a mathematical model involving calculus into a form that can be solved with a computer requires special technique. For this model of isotopic diffusion we rely on the Crank-Nicholson technique for solution of a second-order partial differential equation and an efficient algorithim for the inversion of the equation.

The main equation used is the following:

$$\frac{\partial \delta}{\partial t} = \frac{D_f \rho_v}{\rho_f} \frac{\partial^2 \delta}{\partial z^2} \qquad \text{(a1)}$$

For simplicity the factor $\frac{D_f \rho_v}{\rho_f}$ which is the effective diffusivity is called C:

$$C = \frac{D_f \rho_v}{\rho_f} \qquad \text{(a2)}$$

The Crank-Nicholson technique works in the following manner. We approximate a time interval and rewrite the L.H.S. of equation (a1) as:

$$\frac{\partial \delta}{\partial t} \simeq \frac{\delta_i' - \delta_i}{\Delta t} \qquad \text{(b1)}$$

δ_i' is the new calculated value of δ_i which we must solve for. The R.H.S. using an average of the second derivative with respect to Z becomes:

$$\frac{C}{2}\left(\frac{\delta'_{i+1}-2\delta'_i+\delta'_{i-1}}{\Delta Z^2}+\frac{\delta_{i+1}-2\delta_i+\delta_{i-1}}{\Delta Z^2}\right) \qquad \text{(c1)}$$

Substituting equation (b1) for the L.H.S. of equation (a1) and inserting equation (c1) for the R.H.S. of equation (a1), we form the calculable equation (d1):

$$\frac{\delta'_i-\delta_i}{\Delta t}=\frac{C}{2\Delta Z^2}\left(\delta'_{i+1}-2\delta'_i+\delta'_{i-1}+\delta_{i+1}-2\delta_i+\delta_{i-1}\right) \qquad \text{(d1)}$$

Z is the thicknes of the layer being evaluated.

We now segregate the known and unknown terms with the unknown terms on the L.H.S.:

$$-\delta'_{i+1}\left(\frac{C\Delta t}{2\Delta Z^2}\right)+\delta'_i\left(1+\frac{C\Delta t}{\Delta Z^2}\right)+\delta'_{i-1}\left(\frac{C\Delta t}{2\Delta Z^2}\right)=\delta_{i+1}\left(\frac{C\Delta t}{2\Delta Z^2}\right)+\delta_i\left(1-\frac{C\Delta t}{\Delta Z^2}\right)+\delta_{i-1}\left(\frac{C\Delta t}{2\Delta Z^2}\right) \qquad \text{(e1)}$$

This equation applies except for the endpoints. The two extreme cases must be treated specially.

The delta values for the upper and lower boundaries are taken as constant to facilitate calculation of the intervening values. At i=2 δ'_1 and i=n-1 δ'_n , are known and should be moved to the R.H.S. This produces equations (f1) and (g1):

$$i=2,\quad -\delta'_{i+1}\left(\frac{C\Delta t}{2\Delta Z^2}\right)+\delta'_i\left(1+\frac{C\Delta t}{\Delta Z^2}\right)=\delta_{i+1}\left(\frac{C\Delta t}{2\Delta Z^2}\right)+\delta_i\left(1-\frac{C\Delta t}{\Delta Z^2}\right)+\delta_{i-1}\left(\frac{C\Delta t}{2\Delta Z^2}\right)+\delta'_{i-1}\left(\frac{C\Delta t}{2\Delta Z^2}\right) \qquad \text{(f1)}$$

$$i=n,\quad \delta'_i\left(1+\frac{C\Delta t}{\Delta Z^2}\right)-\delta'_{i-1}\left(\frac{C\Delta t}{2\Delta Z^2}\right)=\delta_{i+1}\left(\frac{C\Delta t}{2\Delta Z^2}\right)+\delta_i\left(1-\frac{C\Delta t}{\Delta Z^2}\right)+\delta_{i-1}\left(\frac{C\Delta t}{2\Delta Z^2}\right)+\delta'_{i+1}\left(\frac{C\Delta t}{2\Delta Z^2}\right) \qquad \text{(g1)}$$

Equation (f1) is the first in the matrix, equation (g1) the last. The matrix forms a system of n-2 equations in n-2

unknowns $(\delta_2' \rightarrow \delta_{n-1}')$ which is readily solved for δ_i' . The program is incremented forward through time.

APPENDIX B
COMPUTER CODE

```
      $JOB
C
C
C           THIS COMPUTER PROGRAM IS BEING UNDERTAKEN WITH
C           THE LOFTY GOAL OF SIMULATING DELTA SMOOTHING
C           PROFILES IN FIRN. THIS WILL BE ACCOMPLISHED BY
C           USE OF THE CRANK-NICHOLSON TECHNIQUE AND SOLUTION
C            OF A MATRIX INVERSION. GOD SAVE THE QUEEN.
C
      1     DIMENSION DELTA(40),A(40),B(40),CC(40),D(40),TDELTA(20)
      2     REAL BB(40),G(40)
C
C           NDEPTH IS THE NUMBER OF DEPTH STEPS (ZSTEP).
C           THE TOTAL DEPTH IS EQUAL TO (NDEPTH-1)*ZSTEP.
C
      3       NDEPTH=40
C
      4          NDEP1=NDEPTH-1
C
C           ZSTEP IS EQUAL TO THE DEPTH STEP IN METERS.
C
      5       ZSTEP=0.05
C
C           TSTEP IS TIME INCREMENT IN SECONDS
      6       TSTEP=0.25E7
C
C           NTIMES IS THE NUMBER OF TSTEP INCREMENTS
      7     NTIMES=280
C
C           THIS LOOP READS IN THE DELTA VALUES
C
      8       WRITE(6,400)
C
      9       DO 20 I=1,20
C
     10     READ(5,69)TDELTA(I)
C
     11  20   CONTINUE
C
     12     IDETAL=NDEPTH/20
     13     DO 96 I=1,20
     14     DO 96 J=1,IDETAL
     15     JJ=(I-1)*IDETAL+J
     16     DELTA(JJ)=TDELTA(I)
     17  96 CONTINUE
C
C
     18       WRITE(6,300)TDELTA
C
C
     19         DO 5000 ITIMES=1,NTIMES
C
```

```
20          DO 4000 I=2,NDEP1
C                 ZZ IS THE DEPTH OF THE INTERVAL IN QUESTION
C                 AND IS EQUAL TO THE DEPTH STEP INCREMENT* # OF STEPS
21          ZZ=I*ZSTEP
C               YEARS IS THE TIME INTERVAL BETWEEN DEPOSITION OF THE
C               SNOW AND THE PRESENT. YEARS IS IN YEARS.
22          YEARS=ITIMES*TSTEP/3.15E7
C           SECOND IS THE TOTAL TIME IN SECONDS
23          SECOND=YEARS*3.15E7
C                C IS THE EFFEECTIVE DIFFUSIVITY OF THE FIRN IN
C                METER**2/S??
24        CTEM=T(ZZ,YEARS)
25          C=CCC(T(ZZ,YEARS))
C
CC               A, B, CC,  ARE ELEMENTS IN THE NORMAL MATRIX
C
26          A(I)=-(C*TSTEP/(2.*ZSTEP**2))
27          B(I)=1+(C*TSTEP/ZSTEP**2)
28          CC(I)=-(C*TSTEP/(2.*ZSTEP**2))
C               D(I) IS THE SUM OF THE ALREADY KNOWN DELTA WITH
C           THEIR ELEMENTS. IN ORDER TO CALCULATE D(2) AND
C           D(NDEPI) WHICH ARE SPECIAL CASES WE SPECIFY
C           THAT   DELTA(1) AND DELTA(NDEP1) RESPEC-
C           TIVELY DO NOT CHANGE.
29          D(I)=(-A(I)*DELTA(I-1))+((-C*TSTEP/ZSTEP**2)*DELTA(I))
C         C+DELTA(I)-(CC(I)*DELTA(I+1))
C
30       4000   CONTINUE
C               THE FOLLOWING SUPERCEDES D(2) AND D(NDEP1)
C
31          D(2)=+(C*TSTEP/(2.*ZSTEP**2))*(DELTA(1)+DELTA(1))
C
32          D(2)=D(2)+DELTA(2)-(C*TSTEP/ZSTEP**2)*DELTA(2)
C
33          D(2)=D(2)+((C*TSTEP/(2.*ZSTEP**2))*DELTA(3))
C
C               D(NDEP1)
C
34          D(NDEP1)=(C*TSTEP/(2.*ZSTEP**2))*DELTA(NDEP1-1)
```

```
      C
   35 C          D(NDEP1)=D(NDEP1)+DELTA(NDEP1)-(C*TSTEP/ZSTEP**2)*DELTA(NDEP1)
      C
   36 C          OOPS=DELTA(NDEPTH)+DELTA(NDEPTH)
      C
   37 C          D(NDEP1)=D(NDEP1)+(C*TSTEP/(2.*ZSTEP**2))*OOPS
      C
      C               THIS LOOP COMPUTES THE ELEMENTS AND SOLVES
      C
      C               THE MATRIX MADE UP OF THE NDEPTH EQUATIONS.
      C
   38 C          BB(2)=CC(2)/B(2)
   39            G(2)=D(2)/B(2)
   40            DO 2000 K=3,NDEP1
   41            BB(K)=CC(K)/(B(K)-A(K)*BB(K-1))
   42            G(K)=(D(K)-A(K)*G(K-1))/(B(K)-A(K)*BB(K-1))
   43  2000      CONTINUE
   44            DELTA(NDEP1)=G(NDEP1)
      C
      C                 THIS LOOP COMPUTES THE NEW DELTA ARRAY
      C
      C
      C
   45            NDEP2=NDEPTH-2
   46            DO 3000 J=2,NDEP2
   47            K=NDEPTH-J
   48            DELTA(K)=G(K)-BB(K)*DELTA(K+1)
   49  3000      CONTINUE
      C
   50            DO 90 I=1,20
   51            TDELTA(I)=0.0
   52           DO 89 J=1,IDETAL
   53           JJ=(I-1)*IDETAL+J
   54    89     TDELTA(I)=TDELTA(I)+DELTA(JJ)
   55    90     TDELTA(I)=TDELTA(I)/IDETAL
   56            C=CCC(T(0.0,YEARS))
   57            TEM=T(0.0,YEARS)
      C
   58            WRITE(6,600)YEARS,TEM,C
   59            WRITE(6,500)TDELTA
   60            WRITE(6,500)DELTA
   61   5000     CONTINUE
   62     69     FORMAT(F7.2)
   63    600     FORMAT(' ',2(F10.5),E13.5)
      C
   64    500     FORMAT(' ',10(F7.2))
   65    400     FORMAT('1')
   66    300     FORMAT(' ',10(F10.5))
   67            STOP
   68            END
      C
      C
```

*** WATFIV CROSS REFERENCE ***

*** '#' INDICATES VARIABLE DID NOT APPEAR IN A TYPE STATEMENT

REFERENCES TO VARIABLES

```
*A*# 1 26 29 41 42   *B*# 1 27 38 39 41 42   *BB*  2 38 41 42 48   *C*# 25
*CC*# 1 28 29 38 41   *CCC*# 25 56   *CTEM*# 24   *D*# 1 29 31 32 33 34 35
    44 48 54 60   *G*  2 39 42 44 48   *I*# 9 10 13 15 16 20 21 26 27 28 29
*ITIMES*# 19 22   *J*# 14 15 46 47 52 53   *JJ*# 15 16 53 54   *K*# 40 41 42
*NDEP1*# 4 20 34 35 37 40 44   *NDEP2*# 45 46   *NTIMES*# 7 19   *OOPS*# 36
*TDELTA*# 1 10 16 18 51 54 55 59   *TEM*# 57 58   *TSTEP*# 6 22 26 27 28 29
    57 58   *ZSTEP*# 5 21 26 27 28 29 31 32 33 34 35 37   *ZZ*# 21 24 25

    REFERENCES TO STATEMENT NUMBERS

*20*  9 11   *69*  10 62   *89*  52 54   *90*  50 55   *96*  13 14 17   *300
*600*  58 63   *2000*  40 43   *3000*  46 49   *4000*  20 30   *5000*  19 61

                                        *** END OF WATFIV CROSS REFERENCE

69          FUNCTION CCC(T)
C                THIS IS FUNCTION SUBPROGRAM CCC(T) FOR DIFFUSIVITY
70          REAL MW
C
C                DA IS DIFFUSIVITY OF WATER VAPOR IN AIR  IN M**2/A
71          DA=(0.0371*(T+273.16)**1.75)/3.15E7
C
C
C                DENF IS THE DENSITY OF THE FIRN  KG/M**2
72          DENF=400.
C
C                DENC IS THE DENSITY OF FIRN AT CLOSE OFF KG/M**2
73          DENC=830.
C
C                PS IS THE PROPORTION OF PORE SPACE
74          PS=1-DENF/DENC
C
C                DF IS THE DIFFUSIVITY OF THE FIRN M**2/A
75          DF=DA*PS
C
C                P IS THE PARTIAL PRESSURE OF WATER VAPOR IN AIR
76          P=10**(10.5553-(2667/(T+273.0)))*100
C
C
C                 R IS THE GAS CONSTANT IN  J/MOLE*K
C
77          R=8.314
C
C
C           MW IS THE MOLECULAR WEIGHT IN KG ?
78          MW=.018
C
C                DENV IS THE DENSITY OF THE WATER VAPOR IN KG/M**3
C
79          DENV=(P*MW)/(R*(T+273.16))
C
C
C
C                CCC IS THE EFFECTIVE DIFFUSIVITY OF WATER VAPOR
C                IN FIRN WITH RESPECT TO TEMPERATURE AND DEPTH
C
80          CCC=((DF*DENV)/DENF)
C
C
```

```
      RETURN
      END
```

*** WATFIV CROSS REFERENCE ***

*** '#' INDICATES VARIABLE DID NOT APPEAR IN A TYPE STATEMENT

REFERENCES TO VARIABLES

CCC# 69 80 *DA*# 71 75 *DENC*# 73 74 *DENF*# 72 74 80 *DENV*# 79 8
PS# 74 75 *R*# 77 79 *T*# 69 71 76 79

*** END OF WATFIV CROSS REFERENCE

```
      FUNCTION T(ZZ,YEARS)
      REAL KK
C
C     TO=-21  WHICH IS THE MEAN ANNUAL TEMPERATURE
      TO=-21
C
C     A IS THE ANNUAL TEMP AMPLITUDE
      A=15
      OMEGA=2*3.14159
C
C
      FAC=-ZZ*(OMEGA/(2.*13.))**0.5
C
      T=A*EXP(FAC)*(COS(OMEGA*YEARS+FAC))+TO
C
C
      RETURN
      END
C
C
```

*** WATFIV CROSS REFERENCE ***

*** '#' INDICATES VARIABLE DID NOT APPEAR IN A TYPE STATEMENT

REFERENCES TO VARIABLES

A# 86 89 *COS*# 89 *EXP*# 89 *FAC*# 88 89 *KK* 84 *OMEGA*# 87 8
89 *ZZ*# 83 88

*** END OF WATFIV CROSS REFERENCE

```
      $ENTRY
```

REFERENCES

Atkins, P. W. 1978. Physical Chemistry. Oxford University Press; 1018 p.

Benson, C. S. 1962. Stratigraphic Studies in the snow and firn of the Greenland Ice Sheet. Research Report 70 July 1962 U.S. Army Snow Ice and Permafrost Research Est.

Bow, W. 1982. Isotopic Diffusion In Polar Firn. Masters Thesis Ohio State University, Unpublished.

CRC 1982. Handbook of Chemistry and Physics, 62 nd edition. Chemical Rubber Publishing Company, Boca Raton, Florida, U.S. of A.

Geiger, G. H. and Poirier D. R. 1973. Transport Phenomena in Metallurgy. Addison-Wesley Publishing Company, Reading, Massachusetts, U.S. of A. page 467.

Iribarne and Godson 1973. Atmospheric Thermodynamics. Geophysical and Astrophysical Monographs Volume 6. D. Reidel Publishing Company, Boston, Massachusetts, U.S. of A. page 60-63

Johnsen S. 1977. Stable Isotope homogenization of polar firn and ice. Isotopes and Impurities in Snow and Ice: Proceedings of the Grenoble Symposium, August/ September 1975. IAHS-AISM Publication no. 18, pages 159-163.